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(54) POLYOXYMETHYLENE RESIN COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a polyoxymethylene resin composition exhibiting good affinity and dispersibility of a polyoxymethylene resin and a styrene resin, a polycarbonate resin and a polyolefin resin, having excellent dimensional stability, mechanical properties such as impact resistance and thermal stability and giving a molded article having excellent surface state.

SOLUTION: The objective polyoxymethylene resin composition is produced by compounding 100 pts.wt. of a polyoxymethylene resin obtained by the copolymerization of trioxane and 1,3-dioxolane in the presence of a cationic active catalyst, using 7.1-11.0 mol% of 1,3-dioxolane based on trioxane and having a crystallization time of 30-600 sec at 148°C with 0-100 pts.wt. of at least one kind of resin selected from styrene resin, polycarbonate resin and polyolefin resin.

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the polyoxymethylene resin constituent which especially the dispersibility was good to polyoxymethylene resin, excelled [resin] in the surface state of mold goods, and was excellent in it at mechanical properties, such as dimensional stability and shock resistance, and thermal stability about the molding resin constituent which blended styrene resin, polycarbonate system resin, or polyolefine system resin.

[0002]

[Description of the Prior Art] Polyoxymethylene resin has the property which was excellent in a mechanical property, a thermal property, electrical characteristics, sliding nature, a moldability, etc., and is widely used for an electrical machinery and apparatus, autoparts, a precision machinery component, etc. as a structural material, a mechanism element, etc.

[0003] However, although polyoxymethylene resin has high crystallinity therefore, its molding shrinkage is high, and with the components as which advanced dimensional accuracy is required, it produces curvature and deformation and has the problem that demand dimensional accuracy is difficult to get. Moreover, mechanical physical properties, such as shock resistance, may not be enough, and require still much more improvement depending on an application in many cases.

[0004] By the way, generally, it has the property to compensate the physical properties, and also to reforming of the physical properties of thermoplastics, blending resin and compensating the fault is usually performed, and the purpose is attained to it in many cases.

[0005] However, polyoxymethylene resin has compatibility mutual [between resin], and especially bad dispersibility, when blending other thermoplastics unlike common thermoplastics, when adhesion of the interface of a bi-phase is also inadequate, produces the phase separation in an interface and is used as mold goods, surface exfoliation may be produced and reforming by the combination means of these other resin is very difficult.

[0006] Although styrene resin and polycarbonate system resin are amorphism nature, and it is thermoplastics with small molding shrinkage and especially polyolefine system resin is combination resin which fitted lightweight-ization most for low specific gravity, when the combination to these resin of adhesion of the interface of a bi-phase instead of an exception is also inadequate, and the phase separation in an interface is produced and it considers as mold goods, there is a problem practically, such as being easy to produce surface exfoliation.

[0007] For this reason, although it is the purpose which improves the compatibility of polyoxymethylene resin and these resin, for example, the approach (JP,64-38463,A) of making the specific range the ratio of the melt flow value of polyoxymethylene resin and styrene resin, the approach (JP,59-64654,A) of blending with polyoxymethylene resin the polyolefine system resin which contains a reactant glycidyl group in the molecular structure, the approach (JP,59-204652,A) of blending the denaturation alpha olefin system polymer which comes to carry out the graft copolymerization of the unsaturated carboxylic acid, etc. are proposed, it has not resulted in still sufficient improvement.

[0008] Moreover, polyoxymethylene resin is lacking in the molecular structure top thermal stability, and decomposing easily by principal chain cutting by the depolymerization and the thermal oxidation reaction from a polymer end is known. Furthermore, it is promoted in the case of melting kneading for example, with other resin, and this thermal oxidation decomposition reaction may spoil the thermal stability of polyoxymethylene resin greatly.

[0009]

[Problem(s) to be Solved by the Invention] The technical problem which this invention tends to solve has the compatibility of polyoxymethylene resin, and styrene resin, polycarbonate system resin or polyolefine system resin, and dispersibility in offering the polyoxymethylene resin constituent which was good, was excellent in the surface state of mold goods, and was excellent in mechanical properties, such as dimensional stability and shock resistance, and thermal stability.

[0010]

[Means for Solving the Problem] In copolymerizing 1 of a trioxane and the amount of specification, and 3-dioxolane, as a result of inquiring wholeheartedly that this invention persons should solve the above-mentioned technical problem As opposed to the polyoxymethylene resin which is obtained by considering as specific polymerization time amount and which is the crystallization time amount of the specific range It came to complete a header and this invention for attaining the above-mentioned purpose by blending at least one sort chosen from styrene resin, polycarbonate system resin, and polyolefine system resin.

[0011] Namely, it hits that this invention copolymerizes a trioxane and 1 and 3-dioxolane using a cation activity catalyst. As opposed to the polyoxymethylene resin 100 weight section whose crystallization time amount [in / it is used and obtained and / 148 degrees C] is 30 - 600 seconds 1 and 3-dioxolane -- a trioxane -- receiving -- 7.1-11.0-mol % -- At least one sort chosen from styrene resin, polycarbonate system resin, and polyolefine system resin is related with the polyoxymethylene resin constituent which comes to blend the 0 - 100 weight section.

[0012]

[Embodiment of the Invention] The polyoxymethylene resin used by this invention is obtained by carrying out the polymerization of the trioxane which is the annular trimer of the formaldehyde as a raw material monomer, and 1 as a comonomer and 3-dioxolane to the bottom of existence of a cationic polymerization catalyst. 1 in this case and the addition of 3-dioxolane are 7.1-11.0-mol % to a trioxane. When there is less amount of 1 and 3-dioxolane used than this, the dispersibility between resin made into the purpose of this invention is bad, and when many, the property of resin original is lost and it is not desirable.

[0013] A general cation activity catalyst is used as a polymerization catalyst. as such a cation activity catalyst -- Lewis acid -- especially -- boron and tin -- Halogenides, for example, a boron trifluoride, such as titanium, Lynn, an arsenic, and antimony A tin tetrachloride, a titanium tetrachloride, a phosphorus pentachloride, phosphorus pentafluoride, arsenic pentafluoride, and 5 antimony fluoride, And the complex compound or the compound like a salt, and proton acid, for example, trifluoro methansulfonic acid, the ester of a PAKURORU acid and proton acid -- especially -- the ester of the Per Krol acid and low-grade fatty alcohol -- The anhydride of proton acid, especially the mixed anhydride of the Per Krol acid and low-grade aliphatic carboxylic acid, Or triethyl oxonium hexafluoro phosphate, triphenylmethyl hexafluoro ARUZENATO, acetyl hexafluoro borate, a heteropolyacid or its acid salt, an isopolyacid, or its acid salt is mentioned. The compound containing especially a boron trifluoride or a boron-trifluoride hydrate, and a coordinated complex compound are suitable, and especially boron-trifluoride JIECHIRUE-Thera-TO and boron-trifluoride dibutyl etherate that are a coordinated complex with ether are desirable.

[0014] The polymerization method of polyoxymethylene resin can be conventionally performed by the same facility and same approach as copolymerization of a well-known trioxane. That is, either a batch type or continuous system is possible, and it is applied also to the polymerization method performed under existence of an organic solvent like a bulk polymerization or a cyclohexane. In a batch type, a reaction vessel with an agitator can be used and equipments, such as powerful stirring capacity that the

rapid solidification at the time of a polymerization and generation of heat can be coped with, precise temperature control, a kneader having the self-cleaning function to prevent adhesion of a scale further, a 2 shaft screw-type continuous extrusion kneading machine, and a paddle mold continuous mixer of two shafts, are suitably used in a continuous system bulk polymerization.

[0015] In the polymerization of polyoxymethylene resin, control of the polymerization temperature before and behind 60 - 90% of polymerization yield (it is defined as boundary yield) is important. Boundary yield is 80 - 90% 70 to 90% 65 to 90% preferably. Polymerization temperature should be kept it is desirable, is more desirable at 60-110 degrees C, and the most desirable at 60-100 degrees C at 60-120 degrees C by the range of 60-90 degrees C until polymerization yield reaches boundary yield. Moreover, polymerization yield should be kept it is desirable, is more desirable at 0-80 degrees C, and the most desirable at 0-70 degrees C at 0-100 degrees C by the range of 0-60 degrees C more than boundary yield. If polymerization temperature until polymerization yield reaches boundary yield is higher than this, thermal stability will fall and polymerization yield will also fall. Moreover, although thermal stability is held when low, polymerization yield falls also in this case. When the polymerization temperature more than boundary yield is higher than this, thermal stability falls, and when low, unarranging, such as causing the torque rise of the power requirement for agitation and mixing of a polymerization machine, occurs. Moreover, the polymerization temperature more than boundary yield must not become higher than temperature until it reaches boundary yield. If this is reversed, thermal stability falls.

[0016] In the polymerization of polyoxymethylene resin, it is desirable for the polymerization time amount for 3 - 120 minutes to be chosen, and to consider as 10 - 60 minutes especially. When polymerization time amount is shorter than this, thermal stability falls.

[0017] The polyoxymethylene resin therefore obtained at the polymerization reaction performs deactivation-izing of a catalyst, and removal processing for quenchers, such as a trivalent organic phosphorous compound, an amine compound, and a hydroxide of alkali metal or alkaline earth metal, by independent or the well-known approach of using it with the gestalt of a water solution or an organic solution. Especially a trivalent organic phosphorous compound and the trivalent third class amine are preferably used in these.

[0018] Although it can send to a latter stabilization process as it is, if the polyoxymethylene resin which performed deactivation-ization of a polymerization catalyst needs much more purification, it can pass through washing, separation recovery of an unreacted monomer, desiccation, etc. To a stable chemically-modified degree, stabilizers, such as an antioxidant and a thermostabilizer, are blended, melting kneading is carried out with a twin screw extruder etc., and stabilizing treatment is carried out to polyoxymethylene resin.

[0019] On the occasion of stabilizing treatment, steric hindrance nature phenols, such as triethylene glycol-screw-3-(3-t-butyl-4-hydroxy-5-methylphenyl) propionate and pentaerythrityl-tetrakis-3-(3, 5-G t-butyl-4-hydroxyphenyl) propionate, are mentioned as an anti-oxidant which can be used. As a thermostabilizer, sodium, such as amine permutation triazine, such as a melamine, methylol melamine, benzoguanamine, cyanoguanidine, N, and N-diaryl melamine, polyamides, a urea derivative, and urethane, and a potassium, calcium, magnesium, the inorganic-acid salt of barium, a hydroxide, an organic-acid salt, etc. are mentioned.

[0020] In addition, the crystallization time amount in 148 degrees C of the obtained polyoxymethylene resin is 30 - 600 seconds. A good resin constituent is obtained by making the crystallization time amount of the resin with which this invention is presented adjust to this range. When crystallization time amount is short, the effectiveness of this invention is not demonstrated enough, but when too long, the property of polyoxymethylene resin will be spoiled.

[0021] next, as styrene resin used in this invention Styrene, alpha methyl styrene, vinyltoluene, p-tert-butyl styrene, Aromatic series vinyl compounds, such as p-hydroxystyrene, and the homopolymer of the derivative, Or the random and block which consist of these two or more sorts, or a graft copolymer, To these, or derivatives, such as alpha, such as an acrylic acid and a methacrylic acid, beta-partial saturation acid, or its ester, Vinyl ester, such as acrylonitrile, methacrylonitriles and these derivatives, or vinyl

acetate, The random which comes to contain more than a kind of the comonomer components, such as vinyl ether, such as vinyl methyl ether, and a derivative of these vinyl system compounds, a block, or a graft copolymer is mentioned, and how, such as the polymerization degree, a side chain, the existence of branching or extent, and a copolymerization presentation ratio, is not asked.

[0022] Styrene system copolymerization resin is desirable especially in these, and, as for the copolymer which has effectiveness in dimensional stability, the hydrogenation object of a styrene acrylonitrile copolymer, a styrene acrylic-acid methyl ester copolymer, a styrene methacrylic-acid-methylester copolymer, a styrene acrylonitrile butadiene copolymer, and a styrene acrylonitrile butadiene copolymer, a styrene acrylonitrile ethylene copolymer, etc. are mentioned. Moreover, as what has effectiveness in shock resistance, the hydrogenation object of the hydrogenation object of a styrene acrylonitrile butadiene copolymer and a styrene acrylonitrile butadiene copolymer, a styrene butadiene block copolymer, and a styrene butadiene block copolymer, a styrene acrylonitrile ethylene copolymer, etc. are mentioned.

[0023] As polycarbonate system resin, the phosgene method or a bivalence hydroxy compound, and carbonic acid diester are used as a raw material, and it is obtained by the ester interchange method which carries out melt polycondensation. It is not limited by these manufacturing methods although furthermore obtained also by the solid-state-polymerization method. The aliphatic series and aromatic series which have a repeat carbonate radical [being fundamental (-OCOO-)], and an aliphatic series-aromatic series polycarbonate are usable. Usually, aromatic series polycarbonate resin has desirable polycarbonate resin of a 2 and 2-bis(4-hydroxyphenyl) propane known as bisphenol A mold polycarbonate resin. In consideration of a mechanical strength and a moldability, the thing of 10,000-40,000 has [polycarbonate system resin] desirable viscosity average molecular weight.

[0024] As polyolefine system resin, ethylene, a propylene, a butene, a hexene, The homopolymer of alpha olefins, such as octene, nonene, decene, and dodecen, Or the random and block which consist of these two or more sorts, or a graft copolymer, To these, or 1, 4-hexadiene, a dicyclopentadiene, 5-ethylidene-2-norbornene, Nonconjugated diene, such as 2 and 5-NORUBONA diene, a butadiene, an isoprene, Derivatives, such as alpha, such as conjugated diene components, such as piperylene, an acrylic acid, and a methacrylic acid, beta-partial saturation acid, or its ester, Aromatic series vinyl compounds, such as acrylonitrile, styrene, and alpha methyl styrene, Or the random which comes to contain more than a kind of the comonomer components, such as vinyl ether, such as vinyl ester, such as vinyl acetate, and vinyl methyl ether, and a derivative of these vinyl system compounds, A block or a graft copolymer is mentioned and how, such as the polymerization degree, a side chain, the existence of branching or extent, and a copolymerization presentation ratio, is not asked.

[0025] these loadings -- the polyoxymethylene resin 100 weight section -- receiving -- the 1 - 100 weight section -- it is 10 - 90 weight section preferably. When loadings are too low, the effectiveness of this invention is not demonstrated enough, but when many [too], the property of polyoxymethylene resin will be spoiled.

[0026] Since a desired property is given, coloring agents, such as various stabilizers, such as a well-known additive, for example, an antioxidant, a thermostabilizer, a weathering (light) stabilizer, and a hydrolysis stabilizer, lubricant, lubricant, a nucleating additive, and dyes and pigments, a release agent, an antistatic agent, a plasticizer, a flame retarder, etc. can be conventionally blended with the resin constituent of this invention. Moreover, the thermoplastics of further others can also be blended in the range which does not spoil the range of this invention.

[0027] The method of preparation of the polyoxymethylene resin constituent of this invention is possible by various well-known approaches. For example, after mixing each component with blenders, such as a turn bull mixer and a Henschel mixer, the approach of kneading with a monopodium or a twin screw extruder, a van PARI mixer, a roll, etc. is chosen suitably. As for each component, drying beforehand before kneading is desirable.

[0028]

[Example] Although an example and the example of a comparison are shown in order to explain this invention concretely below, this invention is not limited to these. In addition, the vocabulary and

measuring method in an example and the example of a comparison are shown below.

[0029] The check of dispersibility and an interface adhesive property: The fracture surface of the piece of shaping was observed with the electron microscope, and the situation of the plainness (it is inferior to dispersibility and an interface adhesive property, so that it is clear) of an interface, a particle distribution gestalt (particle shape, size), and the fracture surface estimated. These were synthesized, and it was ranked and made A, good, and a defect.

Surface friction test: After sticking the Scotch tape (trademark) on the test piece front face and tearing off on certain conditions, viewing estimated the exfoliation situation of a mold-goods surface, O and the thing which exfoliated slightly were made into **, and what exfoliated notably was made into x for what did not exfoliate at all.

Izod impact test: ASTM According to D256, impact strength with a notch (thickness of 3.2mm) was measured.

Molding-shrinkage measurement: ASTM Contraction of mold goods was measured according to D955.

Stagnation thermal stability: Using the injection molding machine which has the clamping pressure of 75ton, fixed time amount stagnation was carried out into the cylinder at 240 degrees C of cylinder temperatures, and the necessary residence time until a silver streak occurs was measured. It is shown that thermal stability is so good that a value is large.

Crystallization time amount: It measured with the polymer crystallization rate measuring device (MKmade from hexa chemistry Inc.- 701) which detects change of the birefringence by crystallization optically. Dipped the film sample with a thickness of about 50 micrometers created with a heat press in the 148-degree C oil bath after heating melting for 2 minutes at 200 degrees C, the light which let the polarizing plate (polarizer) pass for this was made to penetrate, the photo detector detected the quantity of light after polarizing plate (analyzer) passage of this transmitted light, and the time amount which results in crystallization from time amount change of the quantity of light was measured. Here, the sum total of the induction period time amount from measurement initiation at 148 degrees C to crystallization initiation and semi-crystallization time amount (one half of the time amount required by crystallization termination from crystallization initiation) was measured, and this was made into crystallization time amount.

Polymerization yield: It filtered, after dipping 20g of copolymers which performed deactivation processing of a catalyst in a 20ml acetone, and the vacuum drying was performed after the acetone washed 3 times until it became constant weight at 60 degrees C. After an appropriate time, it weighed precisely and the following formulas determined polymerization yield.

Polymerization yield = $M1/M0 \times 100$ (however, the weight before M0; acetone processing and M1; weight after acetone processing and desiccation)

[0030] All monomers (a trioxane +1, 3-dioxolane) are received by making boron-trifluoride diethyl etherate into a catalyst in 1 of the amount shown in examples 1-12, the example 1 of reference - the 2 trioxane 100 weight section, and Table 1, and 3-dioxolane. BF3 It carries out. 60 ppm was used, and 500 ppm was used to all monomers by making a methylal into a chain transfer agent, in the kneader (it has a jacket around) of two shafts with the paddle which gets into gear mutually, jacket temperature (polymerization temperature) was set as 65 degrees C, and the polymerization was performed. After the polymerization time amount shown in Table 1 passing, to the amount of catalysts, deactivation processing of the catalyst was carried out with the triphenyl phosphine [of 2 double mol / 5wt(s)% of] benzene solution, it ground, and the polyoxymethylene copolymer was obtained. Polymerization yield was 90% or more, and the limiting viscosity in 60 degrees C was 1.1 - 1.5 dl/g among p-chloroform (alpha pinene addition). Moreover, the triethylene glycol-screw [3-(3-t-butyl-5-methyl-4-hydroxyphenyl) propionate] (Ciba-Geigy make, trade name IRUGA NOx 245) 0.3 weight section, the melamine 0.1 weight section, and the magnesium-hydroxide 0.05 weight section were added in the obtained copolymer 100 weight section as a stabilizer, and preliminary mixing was performed in it using the Henschel mixer. The twin screw extruder with a vent was supplied after this, and under reduced pressure of 160Torr, at 200 degrees C, melting kneading was carried out and it pelletized. The crystallization time amount of the obtained pellet was measured and the result was shown in Table 1. It

blended with said pellet in the amount of rates which showed the styrene resin of the class shown in Table 1 in Table 1, and preliminary mixing was carried out with the Henschel mixer, using the twin screw extruder with a vent, at 190 degrees C of cylinder temperatures, melting kneading was carried out and preparation of a resin constituent pelletized. Subsequently, injection molding was carried out using this pellet, the test piece was produced, and said evaluation was performed. Moreover, it was similarly estimated as examples 1-14 about the case where styrene resin is not blended. The result was combined and was shown in Table 1.

[0031] It carried out like examples 1-14 except considering as the loadings of 1 and the amount of 3-dioxolanes which were shown in one to example of comparison 9 table 1, polymerization time amount, polyoxymethylene resin, and styrene resin. The result was shown in Table 1.

[0032] The amount of ABS plastics was changed and blended in the amount of rates which showed the 1 [same] as 15 to example 18 example 3, or an example 10, the amount of 3-dioxolanes, polymerization time amount, polyoxymethylene resin, and ABS plastics in Table 2, and it carried out like the example 3 or the example 10. The result was shown in Table 2.

[0033] It carried out like examples 15-18 except considering as 1, the amount of 3-dioxolanes, and polymerization time amount which were shown in ten to example of comparison 13 table 2. The result was shown in Table 2.

[0034] Instead of an example 19 - 30 styrene resin, polycarbonate resin (you pyrone S-3000 made from the Mitsubishi engineering plastics) was used, and in the amount of rates which showed 1 and the amount of 3-dioxolanes which were shown in Table 3, polymerization time amount, polyoxymethylene resin, and polycarbonate resin in Table 3, the amount of polycarbonate resin was changed and blended and was performed like examples 1-14. However, using the twin screw extruder with a vent, at 220 degrees C of cylinder temperatures, melting kneading was carried out and preparation of a resin constituent pelletized. The result was shown in Table 3.

[0035] It carried out like examples 1-12 except considering as the loadings of 1 and the amount of 3-dioxolanes which were shown in 14 to example of comparison 22 table 3, polymerization time amount, polyoxymethylene resin, and polycarbonate resin. The result was shown in Table 3.

[0036] Instead of an example 31 - 42 styrene resin, polyolefine system resin was used and it carried out like examples 1-14 except considering as the loadings of 1 and the amount of 3-dioxolanes which were shown in Table 4, polymerization time amount, polyoxymethylene resin, and polyolefine system resin. The result was shown in Table 4.

[0037] It carried out like examples 31-42 except considering as the loadings of 1 and the amount of 3-dioxolanes which were shown in 23 to example of comparison 31 table 4, polymerization time amount, polyoxymethylene resin, and polyolefine system resin. The result was shown in Table 4.

[0038] The amount of polypropylene resin was changed and blended in the amount of rates which showed the 1 [same] as 43 to example 46 example 32, or an example 38, the amount of 3-dioxolanes, polymerization time amount, polyoxymethylene resin, and polypropylene resin in Table 5, and it carried out like the example 32 or the example 38. The result was shown in Table 5.

[0039] It carried out like examples 43-46 except considering as 1, the amount of 3-dioxolanes, and polymerization time amount which were shown in 32 to example of comparison 35 table 5. The result was shown in Table 5.

[0040]

[Table 1]

| | ポリオキシエチレン樹脂 | | | スチレン系樹脂 | | | 分散性、 界面接着性 | 熱履歴試験 | アイソット 衝撃強度 (J/m) | 成形収縮率 (%) | 耐腐蝕安定性 |
|------|---------------------------|-------------|--------------|---------|-----|-----|---------------|-------|------------------------|--------------|--------|
| | DOL量 TOXに対する DOL(%) | 重合時間 (分) | 結晶化時間 (秒) | 重量部 | 重量部 | 重量部 | | | | | |
| 実施例1 | 8.5 | 3 | 150 | 100 | | B-1 | | | | | |
| " 2 | 8.5 | 3 | 150 | 100 | 40 | | | | 62 | 1.9 | 80 |
| " 3 | 8.5 | 3 | 150 | 100 | | 40 | | | 53 | 1.5 | 80 |
| " 4 | 8.5 | 3 | 150 | 100 | | | | | 93 | 1.3 | 80 |
| " 5 | 8.5 | 10 | 150 | 100 | 40 | | | | 83 | 1.3 | 80 |
| " 6 | 8.5 | 10 | 150 | 100 | | 40 | | | 53 | 1.5 | 80 |
| " 7 | 8.5 | 10 | 160 | 100 | | | | | 93 | 1.3 | 80 |
| 比較例1 | 8.5 | 2 | 150 | 100 | 40 | | | | 83 | 1.3 | 80 |
| " 2 | 8.5 | 2 | 150 | 100 | | 40 | | | 18 | 1.7 | 20 |
| " 3 | 8.5 | 2 | 150 | 100 | | | | | 28 | 1.8 | 20 |
| 実施例8 | 10.0 | 3 | 200 | 100 | | | | | 28 | 1.8 | 20 |
| " 9 | 10.0 | 3 | 200 | 100 | 40 | | | | 63 | 1.9 | 80 |
| " 10 | 10.0 | 3 | 200 | 100 | | 40 | | | 54 | 1.5 | 80 |
| " 11 | 10.0 | 3 | 200 | 100 | | | | | 93 | 1.3 | 80 |
| " 12 | 10.0 | 10 | 200 | 100 | 40 | | | | 84 | 1.3 | 80 |
| " 13 | 10.0 | 10 | 200 | 100 | | 40 | | | 54 | 1.5 | 80 |
| " 14 | 10.0 | 10 | 200 | 100 | | | | | 93 | 1.3 | 80 |
| 比較例4 | 10.0 | 2 | 200 | 100 | 40 | | | | 84 | 1.3 | 80 |
| " 5 | 10.0 | 2 | 200 | 100 | | 40 | | | 18 | 1.7 | 20 |
| " 6 | 10.0 | 2 | 200 | 100 | | | | | 30 | 1.8 | 20 |
| 比較例7 | 8.5 | 3 | 100 | 100 | 40 | | | | 28 | 1.8 | 20 |
| " 8 | 8.5 | 3 | 100 | 100 | | 40 | | | 17 | 2.0 | 10 |
| " 9 | 8.5 | 3 | 100 | 100 | | | | | 23 | 2.0 | 10 |
| " 9 | 8.5 | 3 | 100 | 100 | | | | | 22 | -2.0 | 10 |

注) TOX : Nリオキサソ

DOL : 1,3-ジオキソラン

B-1 : ポリスチレン(A&Mスチレン製 HF-77)

B-2 : スチレン・アクリロニトリル・ブタジエン共重合体(ABS樹脂、テクノポリマー製 TECHNO ABS 430)

B-3 : スチレン・ブタジエンブロック共重合体(JSR製 TR-2000)

[0041]

[Table 2]

| | ポリオキシメチレン樹脂 | | | | スチレン系樹脂 | | | 分散性、 界面接着性 | 衝撃耐衝撃試験 | アイゾット 衝撃強度 (J/m) | 成形収縮率 (%) | 滑溜熱安定性 (分) |
|-------|-----------------------------|-------------|--------------|-----|---------|-----|-----|---------------|---------|------------------------|--------------|---------------|
| | DOL量 TOXに対する DOL(モル分) | 重合時間 (分) | 結晶化時間 (秒) | 重量部 | 重量部 | 重量部 | 重量部 | | | | | |
| | | | | | | B-1 | B-2 | B-3 | | | | |
| 実施例15 | 8.5 | 3 | 150 | 100 | 10 | | | | ○ | 75 | 1.6 | 70 |
| " 3 | 8.5 | 3 | 150 | 100 | 40 | | | | ○ | 88 | 1.3 | 80 |
| " 10 | 8.5 | 3 | 150 | 100 | 100 | | | | ○ | 100 | 1.2 | 80 |
| 比較例10 | 8.5 | 2 | 150 | 100 | 10 | | | | △ | 23 | 1.7 | 30 |
| " 2 | 8.5 | 2 | 150 | 100 | 40 | | | | △ | 28 | 1.5 | 20 |
| " 11 | 8.5 | 2 | 150 | 100 | 100 | | | | △ | 29 | 1.4 | 20 |
| 実施例17 | 10.0 | 3 | 200 | 100 | 10 | | | | ○ | 78 | 1.6 | 70 |
| " 10 | 10.0 | 3 | 200 | 100 | 40 | | | | ○ | 93 | 1.3 | 80 |
| " 18 | 10.0 | 3 | 200 | 100 | 100 | | | | ○ | 102 | 1.2 | 80 |
| 比較例12 | 10.0 | 2 | 200 | 100 | 10 | | | | △ | 25 | 1.7 | 30 |
| " 6 | 10.0 | 2 | 200 | 100 | 40 | | | | △ | 27 | 1.5 | 20 |
| " 13 | 10.0 | 2 | 200 | 100 | 100 | | | | △ | 30 | 1.4 | 20 |

注) TOX : トリオキサン

DOL : 1,3-ジオキソラン

B-1 : ポリスチレン(A&Mスチレン製 HF-77)

B-2 : スチレン・アクリロニトリル・ブタジエン共重合体(ABS樹脂、チクノポリマー製 TECHNO ABS 430)

B-3 : スチレン・ブタジエンブロック共重合体(JSR製 TR-2000)

[0042]

[Table 3]

| | ポリオキシエチレン樹脂 | | | | ポリカーボネート樹脂 | | 分散性、 界面接着性 | 表面剥離試験 | 7/10° 衝撃強度 (J/m) | 成形収縮率 (%) | 滞留熱安定性 (分) |
|-------|-----------------------------|-------------|--------------|-----|------------|-----|---------------|--------|------------------------|--------------|---------------|
| | DOL量 TOXに対する DOL(モル%) | 重合時間 (分) | 結晶化時間 (秒) | 重量部 | 重量部 | 重量部 | | | | | |
| 実施例1 | 8.5 | 3 | 150 | 100 | | | — | — | 62 | 1.9 | 60 |
| " 19 | 8.5 | 3 | 150 | 100 | 10 | | 優 | ○ | 99 | 1.5 | 60 |
| " 20 | 8.5 | 3 | 150 | 100 | 40 | | 優 | ○ | 208 | 1.3 | 60 |
| " 21 | 8.5 | 3 | 150 | 100 | 100 | | 優 | ○ | 318 | 1.0 | 60 |
| " 22 | 8.5 | 10 | 150 | 100 | 10 | | 優 | ○ | 99 | 1.5 | 60 |
| " 23 | 8.5 | 10 | 150 | 100 | 40 | | 優 | ○ | 208 | 1.3 | 60 |
| " 24 | 8.5 | 10 | 150 | 100 | 100 | | 優 | ○ | 318 | 1.0 | 60 |
| 比較例14 | 8.5 | 2 | 150 | 100 | 10 | | 良 | △ | 48 | 1.7 | 20 |
| " 15 | 8.5 | 2 | 150 | 100 | 40 | | 良 | △ | 53 | 1.5 | 20 |
| " 16 | 8.5 | 2 | 150 | 100 | 100 | | 良 | △ | 58 | 1.4 | 20 |
| 実施例8 | 10.0 | 3 | 200 | 100 | | | — | — | 63 | 1.9 | 60 |
| " 25 | 10.0 | 3 | 200 | 100 | 10 | | 優 | ○ | 100 | 1.5 | 60 |
| " 26 | 10.0 | 3 | 200 | 100 | 40 | | 優 | ○ | 209 | 1.3 | 60 |
| " 27 | 10.0 | 3 | 200 | 100 | 100 | | 優 | ○ | 322 | 1.0 | 60 |
| " 28 | 10.0 | 10 | 200 | 100 | 10 | | 優 | ○ | 100 | 1.5 | 60 |
| " 29 | 10.0 | 10 | 200 | 100 | 40 | | 優 | ○ | 209 | 1.3 | 60 |
| " 30 | 10.0 | 10 | 200 | 100 | 100 | | 優 | ○ | 322 | 1.0 | 60 |
| 比較例17 | 10.0 | 2 | 200 | 100 | 10 | | 良 | △ | 49 | 1.7 | 20 |
| " 18 | 10.0 | 2 | 200 | 100 | 40 | | 良 | △ | 54 | 1.5 | 20 |
| " 19 | 10.0 | 2 | 200 | 100 | 100 | | 良 | △ | 58 | 1.4 | 20 |
| 比較例20 | 6.5 | 3 | 100 | 100 | 10 | | 不良 | × | 38 | 1.8 | 10 |
| " 21 | 6.5 | 3 | 100 | 100 | 40 | | 不良 | × | 44 | 1.6 | 10 |
| " 22 | 6.5 | 3 | 100 | 100 | 100 | | 不良 | × | 49 | 1.5 | 10 |

注) TOX ; トリオキサン

DOL ; 1,3-ジオキソラン

[0043]

[Table 4]

| | ネオキソラン樹脂 | | | | ネオラック系樹脂 | | | 分散性、 界面接着性 | 表層剥離試験 | 7イット 衝撃強度 | 溶剤耐安定性 |
|-------|---------------------------|-------------|--------------|-----|----------|-----|-----|---------------|--------|--------------|--------|
| | DOL量 TOXに対する DOL(%) | 重合時間 (分) | 結晶化時間 (秒) | 重量部 | 重量部 | 重量部 | 重量部 | | | | |
| | | | | | | | | | | | |
| 実施例1 | 8.5 | 3 | 150 | 100 | | B-1 | B-2 | B-3 | | | (分) |
| " 31 | 8.5 | 3 | 150 | 100 | 40 | | | | — | 62 | 60 |
| " 32 | 8.5 | 3 | 150 | 100 | | | 40 | | 優 | 93 | 60 |
| " 33 | 8.5 | 3 | 150 | 100 | | | | 10 | 優 | 92 | 60 |
| " 34 | 8.5 | 10 | 150 | 100 | 40 | | | | 優 | 88 | 60 |
| " 35 | 8.5 | 10 | 150 | 100 | | 40 | | | 優 | 93 | 60 |
| " 36 | 8.5 | 10 | 150 | 100 | | | | 10 | 優 | 92 | 60 |
| 比較例23 | 8.5 | 2 | 150 | 100 | 40 | | | | 優 | 88 | 60 |
| " 24 | 8.5 | 2 | 150 | 100 | | 40 | | | 良 | 29 | 20 |
| " 25 | 8.5 | 2 | 150 | 100 | | | | 10 | 良 | 28 | 20 |
| 実施例8 | 10.0 | 3 | 200 | 100 | | | | | 良 | 30 | 20 |
| " 37 | 10.0 | 3 | 200 | 100 | 40 | | | | — | 63 | 60 |
| " 38 | 10.0 | 3 | 200 | 100 | | | 40 | | 優 | 94 | 60 |
| " 39 | 10.0 | 3 | 200 | 100 | | | | 10 | 優 | 94 | 60 |
| " 40 | 10.0 | 10 | 200 | 100 | 40 | | | | 優 | 89 | 60 |
| " 41 | 10.0 | 10 | 200 | 100 | | 40 | | | 優 | 94 | 60 |
| " 42 | 10.0 | 10 | 200 | 100 | | | | 10 | 優 | 89 | 60 |
| 比較例26 | 10.0 | 2 | 200 | 100 | 40 | | | | 優 | 28 | 20 |
| " 27 | 10.0 | 2 | 200 | 100 | | 40 | | | 良 | 28 | 20 |
| " 28 | 10.0 | 2 | 200 | 100 | | | | 10 | 良 | 29 | 20 |
| 比較例29 | 6.5 | 3 | 100 | 100 | 40 | | | | △ | 25 | 10 |
| " 30 | 6.5 | 3 | 100 | 100 | | 40 | | | △ | 25 | 10 |
| " 31 | 6.5 | 3 | 100 | 100 | | | | 10 | △ | 27 | 10 |

注) TOX : トリオキサン

DOL : 1,3-ジオキソラン

B-1 : ポリエチレン(三菱化学製 ノバテック HY330)

B-2 : ポリプロピレン(三菱化学製 ノバテック-P MA4)

B-3 : エチレン・α-オレフィンランダム共重合体(三井化学製 タフマーP0660)

[0044]

[Table 5]

| | ポリオキシメチレン樹脂 | | | | ポリオキシ系樹脂 | | | 分散性、 界面接着性 | 数層剥離試験 | アインツ 衝撃強度 (J/m) | 残留安定性 (分) |
|-------|---------------------------|-------------|--------------|-----|----------|-----|-----|---------------|--------|-----------------------|--------------|
| | DOL量 TOXに対する DOL(%) | 重合時間 (分) | 結晶化時間 (秒) | 重量部 | 重量部 | 重量部 | 重量部 | | | | |
| 実施例43 | 8.5 | 3 | 150 | 100 | | | 10 | 優 | ○ | 78 | 60 |
| " 32 | 8.5 | 3 | 150 | 100 | | | 40 | 優 | ○ | 92 | 60 |
| " 44 | 8.5 | 3 | 150 | 100 | | | 100 | 優 | ○ | 108 | 60 |
| 比較例32 | 8.5 | 2 | 150 | 100 | | | 10 | 良 | △ | 26 | 30 |
| " 24 | 8.5 | 2 | 150 | 100 | | | 40 | 良 | △ | 28 | 20 |
| " 33 | 8.5 | 2 | 150 | 100 | | | 100 | 良 | △ | 31 | 20 |
| 実施例45 | 10.0 | 3 | 200 | 100 | | | 10 | 優 | ○ | 79 | 60 |
| " 38 | 10.0 | 3 | 200 | 100 | | | 40 | 優 | ○ | 93 | 60 |
| " 46 | 10.0 | 3 | 200 | 100 | | | 100 | 優 | ○ | 109 | 60 |
| 比較例34 | 10.0 | 2 | 200 | 100 | | | 10 | 良 | △ | 27 | 30 |
| " 27 | 10.0 | 2 | 200 | 100 | | | 40 | 良 | △ | 29 | 20 |
| " 35 | 10.0 | 2 | 200 | 100 | | | 100 | 良 | △ | 32 | 20 |

注) TOX : トリオキサン

DOL : 1,3-ジオキソラン

B-1 : ポリエチレン(三菱化学製 ノバック HY330)

B-2 : ポリプロピレン(三菱化学製 ノバック-P MA4)

B-3 : エチレン・α-オレフィンランダム共重合体(三井化学製 タフマー-P0680)

[0045]

[Effect of the Invention] The polyoxymethylene resin of this invention is the molding resin constituent which was chosen from styrene resin, polycarbonate system resin, and polyolefine system resin and which blended 1 **** at least, and has the description which especially the dispersibility was good, was excellent in the surface state of mold goods, and was excellent in mechanical properties, such as dimensional stability and shock resistance, and thermal stability.

[Translation done.]